

# Calculation of positron binding to silver and gold atoms

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## Abstract

Positron binding to silver and gold atoms was studied using a fully *ab initio* relativistic method, which combines the configuration interaction method with many-body perturbation theory. It was found that the silver atom forms a bound state with a positron with binding energy 123 ( $\pm 20\%$ ) meV, while the gold atom cannot bind a positron. Our calculations reveal the importance of the relativistic effects for positron binding to heavy atoms. The role of these effects was studied by varying the value of the fine structure constant  $\alpha$ . In the non-relativistic limit,  $\alpha = 0$ , both systems  $e^+\text{Ag}$  and  $e^+\text{Au}$  are bound with binding energies of about 200 meV for  $e^+\text{Ag}$  and 220 meV for  $e^+\text{Au}$ . Relativistic corrections for a negative ion are essentially different from that for a positron interacting with an atom. Therefore, the calculation of electron affinities cannot serve as a test of the method used for positron binding in the non-relativistic case. However, it is still a good test of the relativistic calculations. Our calculated electron affinities for silver (1.327 eV) and gold (2.307 eV) atoms are in very good agreement with corresponding experimental values (1.303 eV and 2.309 eV respectively).

## I. INTRODUCTION

Positron binding by neutral atoms has not been directly observed yet. However, intensive theoretical study of the problem undertaken in the last few years strongly suggests that many atoms can actually form bound states with a positron (see, e.g. [1–8]). Most of the atoms studied so far were atoms with a relatively small value of the nuclear charge  $Z$ . It is important to extend the study to heavy atoms. The main obstacle in this way is the rapid rise of computational difficulties with increasing number of electrons. However, as we show in this paper, an inclusion of relativistic effects is also important. The role of these effects in positron binding to atoms has not been truly appreciated. Indeed, one can say that due to strong Coulomb repulsion a positron cannot penetrate to short distances from the nucleus and remains non-relativistic. However, the positron binding is due to interaction with electrons which have large relativistic corrections to their energies and wave functions. The binding energy is the difference between the energies of a neutral atom and an atom bound with a positron. This difference is usually small. On the other hand, relativistic contributions to the energies of both systems are large and there is no reason to expect they are the same and cancel each other. Therefore, some relativistic technique is needed to study positron binding by heavy atoms.

For both light and heavy atoms the main difficulty in calculations of positron interaction comes from the strong electron-positron Coulomb attraction. This attraction leads to virtual positronium (Ps) formation [9]. One can say that it gives rise to a specific short-range attraction between the positron and the atom, in addition to the usual polarizational potential which acts between a neutral target and a charged projectile [1,9–11]. This attraction cannot be treated accurately by perturbations and some all-order technique is needed. In our earlier works [1,9–11] we used the Ps wave function explicitly to approximate the virtual Ps-formation contribution to the positron-atom interaction and predicted  $e^+\text{Mg}$ ,  $e^+\text{Zn}$ ,  $e^+\text{Cd}$  and few other bound states. The same physics may also explain the success of the stochastic variational method in positron-atom bound state calculations (see, e.g. [3] and Refs. therein). In this approach the wave function is expanded in terms of explicitly correlated Gaussian functions which include factors  $\exp(-\alpha r_{ij}^2)$  with inter-particle distances  $r_{ij}$ . Using this method Ryzhikh and Mitroy obtained positron bound states for a whole range of atoms (Be, Mg, Zn, Cu, Ag, Li, Na, K, etc.). This method is well suited for few-particle systems. Its application to heavier systems is done by considering the Hamiltonian of the valence electrons and the positron in the model potential of the ionic core. However, for heavier atoms, e.g., Zn, the calculation becomes extremely time consuming [5], and its convergence cannot be ensured.

Another non-perturbative technique is the configuration interaction (CI) method widely used in standard atomic calculations. This method was applied to the positron-copper bound state in [6]. In this work the single-particle orbitals of the valence electron and positron are chosen as Slater-type orbitals, and their interaction with the  $\text{Cu}^+$  core is approximated by the sum of the Hartree-Fock and model polarization potentials. The calculation shows slow convergence with respect to the number of spherical harmonics included in the CI expansion,  $L_{\text{max}} = 10$  being still not sufficient to extrapolate the results reliably to  $L_{\text{max}} \rightarrow \infty$ .

In their more recent work the same authors applied the CI method to a number of systems consisting of an atom and a positron. These include  $\text{PsH}$ ,  $e^+\text{Cu}$ ,  $e^+\text{Li}$ ,  $e^+\text{Be}$ ,  $e^+\text{Cd}$

and CuPs. In spite of some improvements to the method they still regard it as a “tool with which to perform preliminary investigations of positron binding” [12].

In our previous paper we developed a different version of the CI method for the positron-atom problem [13]. The method is based on the relativistic Hartree-Fock method (RHF) and a combination of the CI method with many body perturbation theory (MBPT). This method was firstly developed for pure electron systems [14] and its high effectiveness was demonstrated in a number of calculations [15–17]. In the paper [13] it was successfully applied to the positron binding by copper. There are several important advances in the technique compared to the standard non-relativistic CI method which make it a very effective tool for the investigation of positron binding by heavy atoms.

1. The method is relativistic in the sense that the Dirac-Hartree-Fock operator is used to construct an effective Hamiltonian for the problem and to calculate electron and positron orbitals.
2.  $B$ -splines [18] in a cavity of finite radius  $R$  were used to generate single-particle basis sets for an external electron and a positron. The  $B$ -spline technique has the remarkable property of providing fast convergence with respect to the number of radial functions included into the calculations [19,20]. Convergence can be further controlled by varying the cavity radius  $R$  while the effect of the cavity on the energy of the system is taken into account analytically [13]. Convergence was clearly achieved for the  $e^+\text{Cu}$  system in Ref. [13] and for the  $e^+\text{Ag}$  and  $e^+\text{Au}$  systems as presented below.
3. We use MBPT to include excitations from the core into the effective Hamiltonian. This corresponds to the inclusion of the correlations between core electrons and external particles (electron and positron) and of the effect of screening of the electron-positron interaction by core electrons. These effects are also often called the polarization of the core by the external particles. We include them in a fully *ab initio* manner up to the second order of the MBPT.

In the present paper we apply this method to the problem of positron binding by silver and gold atoms. Using a similar technique we also calculate electron affinities for both these atoms. Calculations for negative ions serve as a test of the technique used for positron-atom binding. We also study the role of the relativistic effects in neutral silver and gold, silver and gold negative ions and silver and gold interacting with a positron. This is done by varying the value of the fine structure constant  $\alpha$  towards its non-relativistic limit  $\alpha = 0$ .

## II. THEORY

A detailed description of the method was given in Ref. [13]. We briefly repeat it here emphasizing the role of the relativistic effects. We use the relativistic Hartree-Fock method in the  $V^{N-1}$  approximation to obtain the single-particle basis sets of electron and positron orbitals and to construct an effective Hamiltonian.

The two-particle electron-positron wave function is given by the CI expansion,

$$\Psi(\mathbf{r}_e, \mathbf{r}_p) = \sum_{i,j} C_{ij} \psi_i^e(\mathbf{r}_e) \psi_j^p(\mathbf{r}_p), \quad (1)$$

where  $\psi_i^e$  and  $\psi_j^p$  are the electron and positron orbitals respectively. The expansion coefficients  $C_{ij}$  are determined by the diagonalization of the matrix of the effective CI Hamiltonian acting in the Hilbert space of the valence electron and the positron,

$$\begin{aligned} H_{\text{eff}}^{\text{CI}} &= \hat{h}_e + \hat{h}_p + \hat{h}_{ep}, \\ \hat{h}_e &= c\boldsymbol{\alpha}\mathbf{p} + (\beta - 1)mc^2 - \frac{Ze^2}{r_e} + V_d^{N-1} - \hat{V}_{\text{exch}}^{N-1} + \hat{\Sigma}_e, \\ \hat{h}_p &= c\boldsymbol{\alpha}\mathbf{p} + (\beta - 1)mc^2 + \frac{Ze^2}{r_p} - V_d^{N-1} + \hat{\Sigma}_p, \\ \hat{h}_{ep} &= -\frac{e^2}{|\mathbf{r}_e - \mathbf{r}_p|} + \hat{\Sigma}_{ep}, \end{aligned} \quad (2)$$

where  $\hat{h}_e$  and  $\hat{h}_p$  are the effective single-particle Hamiltonians of the electron and positron, and  $\hat{h}_{ep}$  is the effective electron-positron two-body interaction. Apart from the relativistic Dirac operator,  $\hat{h}_e$  and  $\hat{h}_p$  include the direct and exchange Hartree-Fock potentials of the core electrons,  $V_d^{N-1}$  and  $V_{\text{exch}}^{N-1}$ , respectively. The additional  $\hat{\Sigma}$  operators account for correlations involving core electrons.  $\Sigma_e$  and  $\Sigma_p$  are single-particle operators which can be considered as a self-energy part of the correlation interaction between an external electron or positron and core electrons. These operators are often called “correlation potentials” due to the analogy with the non-local exchange Hartree-Fock potential.  $\Sigma_{ep}$  represents the screening of the Coulomb interaction between external particles by core electrons (see [13,14] for a detailed discussion).

To study the role of the relativistic effects we use the form of the operators  $h_e$  and  $h_p$  in which the dependence on the fine structure constant  $\alpha$  is explicitly shown. Single-particle orbitals have the form

$$\psi(\mathbf{r})_{njlm} = \frac{1}{r} \begin{pmatrix} f_n(r)\Omega(\mathbf{r}/r)_{jlm} \\ i\alpha g_n(r)\hat{\Omega}(\mathbf{r}/r)_{jlm} \end{pmatrix}. \quad (3)$$

Then the RHF equations

$$(h_i - \epsilon_n)\psi_n^i = 0, \quad (i = e, p)$$

take the following form

$$\begin{aligned} f'_n(r) + \frac{\kappa_n}{r}f_n(r) - [2 + \alpha^2(\epsilon_n - \hat{V})]g_n(r) &= 0 \\ g'_n(r) - \frac{\kappa_n}{r}g_n(r) + (\epsilon_n - \hat{V})f_n(r) &= 0, \end{aligned} \quad (4)$$

where  $\kappa = (-1)^{l+j+1/2}(j + 1/2)$  and  $V$  is the effective potential which is the sum of the Hartree-Fock potential and correlation potential  $\Sigma$ :

$$\begin{aligned} \hat{V} &= -\frac{Ze^2}{r_e} + V_d^{N-1} - \hat{V}_{\text{exch}}^{N-1} + \hat{\Sigma}_e, \quad \text{- for an electron,} \\ \hat{V} &= \frac{Ze^2}{r_p} - V_d^{N-1} + \hat{\Sigma}_p, \quad \text{- for a positron.} \end{aligned} \quad (5)$$

The non-relativistic limit can be achieved by reducing the value of  $\alpha$  in (4) to  $\alpha = 0$ .

The relativistic energy shift in atoms with one external electron can also be estimated by the following equation [21]

$$\Delta_n = \frac{E_n}{\nu} (Z\alpha)^2 \left[ \frac{1}{j + 1/2} - C(Z, j, l) \right], \quad (6)$$

where  $E_n$  is the energy of an external electron,  $\nu$  is the effective principal quantum number ( $E_n = -0.5/\nu^2$  a.u.). The coefficient  $C(Z, j, l)$  accounts for many-body effects. Note that formula (6) is based on the specific expression for the electron density in the vicinity of the nucleus and therefore is not applicable for a positron.

### III. SILVER AND GOLD NEGATIVE IONS

We calculated electron affinities of silver and gold atoms mostly to test the technique used for positron-atom binding. The calculation of a negative ion  $\text{Ag}^-$  or  $\text{Au}^-$  is a two-particle problem technically very similar to positron-atom binding. The effective Hamiltonian of the problem has a form similar to (2)

$$H_{\text{eff}}^{\text{CI}} = \hat{h}_e(r_1) + \hat{h}_e(r_2) + \hat{h}_{ee},$$

$$\hat{h}_{ee} = \frac{e^2}{|\mathbf{r}_e - \mathbf{r}_p|} + \hat{\Sigma}_{ee},$$

where  $\hat{\Sigma}_{ee}$  represents the screening of the Coulomb interaction between external electrons by core electrons (see Refs. [14,13] for detailed discussion). Electron affinity is defined when an electron can form a bound state with an atom. In this case the difference between the energy of a neutral atom and the energy of a negative ion is called the electron affinity to this atom. Energies of Ag,  $\text{Ag}^-$ , Au,  $\text{Au}^-$  obtained in different approximations and corresponding electron affinities are presented in Table I together with experimental data. The energies are given with respect to the cores ( $\text{Ag}^+$  and  $\text{Au}^+$ ). Like in the case of  $\text{Cu}^-$  [13] the accuracy of the Hartree-Fock approximation is very poor. The binding energies of the 5s electron in neutral Ag and the 6s electron in neutral Au are underestimated by about 21% and 23% respectively, while the negative ions are unbound. Inclusion of either core-valence correlations ( $\Sigma$ ) or valence-valence correlations (CI) does produce binding but the accuracy is still poor. Only when both these effects are included the accuracy for the electron affinities improves significantly becoming 20% for  $\text{Ag}^-$  and 11% for  $\text{Au}^-$ . Further improvement can be achieved by introducing numerical factors before  $\hat{\Sigma}_e$  to fit the lowest  $s$ ,  $p$  and  $d$  energy levels of the neutral atoms. These factors simulate the effect of higher-order correlations. Their values are  $f_s = 0.88$ ,  $f_p = 0.97$ ,  $f_d = 1.08$  for the Ag atom and  $f_s = 0.81$ ,  $f_p = 1$ ,  $f_d = 1.04$  for the Au atom in the  $s$ ,  $p$  and  $d$  channels, respectively. As is evident from Table I, the fitting of the energies of neutral atoms also significantly improves electron affinities. It is natural to assume that the same procedure should work equally well for the positron-atom problem.

Results of other calculations of the electron affinities of silver and gold are presented in Table II together with the experimental values.

#### IV. POSITRON BINDING TO SILVER AND GOLD AND THE ROLE OF RELATIVISTIC EFFECTS

As for the case of copper [13] we have performed calculations for two different cavity radii  $R = 30a_0$  and  $R = 15a_0$ . For a smaller radius convergence with respect to the number of single-particle basis states is fast. However, the effect of the cavity on the converged energy is large. For a larger cavity radius, convergence is slower and the effect of the cavity on the energy is small. When the energy shift caused by the finite cavity radius is taken into account both calculations come to the same value of the positron binding energy. Table III illustrates the convergence of the calculated energies of  $e^+\text{Ag}$  and  $e^+\text{Au}$  with respect to the maximum value of the angular momentum of single-particle orbitals. Energies presented in the table are two-particle energies (in a.u.) with respect to the energies of  $\text{Ag}^+$  and  $\text{Au}^+$ . The number of radial orbitals  $n$  in each partial wave is fixed at  $n = 16$ . Fig. 1 shows the convergence of the calculated energy with respect to  $n$  when maximum momentum of the single-particle orbitals was fixed at  $L = 10$ . The cavity radius in both cases was  $R = 30a_0$ . Table III and Fig. 1 show that even for a larger cavity radius, convergence was clearly achieved. Table III also shows the convergence in different approximations, namely with and without core-valence correlations ( $\Sigma$ ). One can see that while inclusion of  $\Sigma$  does shift the energy, the convergence is not affected.

Table IV shows how positron binding by silver and gold is formed in different approximations. This table is very similar to Table I for the negative ions except there is no RHF approximation for the positron binding. Indeed, the RHF approximation for the negative ions means a single-configuration approximation:  $5s^2$  for  $\text{Ag}^-$  and  $6s^2$  for  $\text{Au}^-$ . These configurations strongly dominate in the two-electron wave function of the negative ions even when a large number of configurations are mixed to ensure convergence. In contrast, no single configuration strongly dominates in the positron binding problem. Therefore we present our results in Table IV starting from the standard CI approximation. In this approximation positron is bound to both silver and gold atoms. However, the inclusion of core-valence correlations through the introduction of the  $\Sigma_e$ ,  $\Sigma_p$  and  $\Sigma_{ep}$  operators shifts the energies significantly. In the case of gold, the  $e^+\text{Au}$  system becomes unbound when all core-valence correlations are included.

As was discussed in our previous paper [13] the dominating factor affecting the accuracy of the calculations is higher-order correlations which mostly manifest themselves via the value of the  $\Sigma$  operator. An introduction of the fitting parameters as described in the previous section can be considered as a way to simulate the effect of higher-order correlations. Also, the energy shift caused by the fitting can be considered as an estimation of the uncertainty of the calculations. This shift is 0.00240 a.u. in the case of silver and 0.00023 a.u. in the case of gold (see Table IV). Note that these values are considerably smaller than energy shifts for the silver and gold negative ions (0.00854 a.u. and 0.00921 a.u. respectively, see Table I). This is because of the cancellation of the effects of the variation of  $\Sigma_e$  and  $\Sigma_p$ . In particular, for gold it is accidentally very small. One can see that even if the value of 0.00240 a.u. is adopted as an upper limit of the uncertainty of the calculations, the  $e^+\text{Ag}$  system remains bound while the  $e^+\text{Au}$  system remains unbound. However, the actual accuracy might be even higher. We saw that the fitting procedure significantly improves the accuracy of the calculations for the silver and gold negative ions. It is natural to assume that the

same procedure works equally well for the positron binding problem. The final result for the energy of positron binding by the silver atom as presented in Table IV is 0.00434 a.u. This result does not include the effect of the finite cavity size. When this effect is taken into account, by means of the procedure described in Ref. [13], the binding energy becomes 0.00452 a.u. or 123 meV. If we adopt the value of 0.00240 a.u. as an estimation of the uncertainty of the result, then the accuracy we can claim is about 20%.

The calculation of the positron binding by copper [13], silver and gold reveal an interesting trend. All three atoms have very similar electron structure. However the positron binding energy for silver (123 meV) is considerably smaller than that for copper (170 meV [13]) while gold atoms cannot bind positrons at all. We believe that this trend is caused by relativistic effects. An argument that the positron is always non-relativistic does not look very convincing because electrons also contribute to the binding energy. Relativistic effects are large for heavy atoms and electron contributions to the positron binding energy could be very different in the relativistic and non-relativistic limits. Indeed, we demonstrated in Ref. [21] that the relativistic energy shift considerably changes the values of the transition frequencies in  $\text{Hg}^+$  ion and sometimes even changes the order of the energy levels. If we use formula (6) with the contribution of the many-body effects  $C = 0.6$ , as suggested in Ref. [21], to estimate the relativistic energy shift for neutral Au then the result is -0.037 a.u. This is about an order of magnitude larger than the energy difference between Au and  $e^+\text{Au}$ . If the relativistic energy shift in  $e^+\text{Au}$  is different from that in Au then the positron binding energy may be strongly affected.

To study the role of the relativistic effects in positron binding in more detail we performed the calculations for Ag,  $\text{Ag}^-$ ,  $e^+\text{Ag}$ , Au,  $\text{Au}^-$  and  $e^+\text{Au}$  in the relativistic and non-relativistic limits. The latter corresponds to the zero value of the fine structure constant  $\alpha$  (see Section II). The results are presented in Table V. One can see that the actual relativistic energy shift for neutral Au is even bigger than is suggested by formula (6) with  $C = 0.6$ . The shift is 0.0805 a.u. which corresponds to  $C = 0.08$ . Formula (6) with  $C = 0.08$  also reproduces the relativistic energy shift for neutral Ag. The relativistic energy shift for an atom with a positron is of the same order of magnitude but a little different in value. This difference turned out to be enough to affect the positron binding energy significantly. In particular, the  $e^+\text{Au}$  system which is unbound in relativistic calculations becomes bound in the non-relativistic limit with binding energy 0.0080 a.u. or 218 meV. In the case of silver, the positron binding energy is considerably higher in the non-relativistic limit. It is 0.0073 a.u. or 199 meV. It is interesting to compare this value with the value of 150 meV obtained by Mitroy and Ryzhikh using the non-relativistic stochastic variational method [4]. Since the convergence was achieved in both calculations the remaining difference should probably be attributed to the different treatment of the core-valence correlations. We use many-body perturbation theory for an accurate calculation of the  $\Sigma$  operator which accounts for these correlations. Mitroy and Ryzhikh use an approximate semi-empirical expression for the  $\Sigma$  operator which is based on its long-range asymptotic behavior.

Note that the relativistic energy shift for negative ions is also large. However electron affinities are less affected. This is because electron affinities are many times larger than positron binding energies and therefore less sensitive to the energy shift. Apart from that there is a strong cancellation between relativistic energy shifts in the negative ion and neutral atom. This means in particular that the calculation of the electron affinities cannot serve as a

test of a non-relativistic method chosen for the positron binding problem. However, it is still a good test of the relativistic calculations. Note also that our calculated relativistic energy shifts for neutral and negative silver and gold are in very good agreement with calculations performed by Schwerdtfeger and Bowmaker by means of relativistic and non-relativistic versions of the quadratic configuration interaction method (see Table VI and Ref. [24]).

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# TABLES

TABLE I. Ground state energies (in a.u.) of silver, gold and their negative ions calculated in different approximations

	Neutral atom	Negative ion	Electron affinity <sup>a</sup>
		Silver	
RHF <sup>b</sup>	-0.22952	-0.20156	-0.02795
RHF + $\Sigma^c$	-0.27990	-0.30231	0.02241
CI <sup>d</sup>	-0.22952	-0.25675	0.02722
CI + $\Sigma_e^e$	-0.28564	-0.33560	0.04996
CI + $\Sigma_e + \Sigma_{ee}^f$	-0.28564	-0.34298	0.05734
CI + $f\Sigma_e + \Sigma_{ee}^g$	-0.27841	-0.32721	0.04880
Experiment <sup>h</sup>	-0.27841	-0.32626	0.04784
		Gold	
RHF <sup>b</sup>	-0.27461	-0.26169	-0.01292
RHF + $\Sigma^c$	-0.34900	-0.41046	0.06146
CI <sup>d</sup>	-0.27461	-0.31369	0.03908
CI + $\Sigma_e^e$	-0.35536	-0.43913	0.08376
CI + $\Sigma_e + \Sigma_{ee}^f$	-0.35536	-0.44943	0.09407
CI + $f\Sigma_e + \Sigma_{ee}^g$	-0.33903	-0.42389	0.08486
Experiment <sup>h</sup>	-0.33903	-0.42386	0.08483

<sup>a</sup>Negative affinity means no binding.

<sup>b</sup>Relativistic Hartree-Fock; a single-configuration approximation, no core-valence correlations are included.

<sup>c</sup>Single-configuration approximation, core-valence correlations are included by means of MBPT.

<sup>d</sup>Standard CI method.

<sup>e</sup>Self-energy part of core-valence correlations are included by adding the  $\Sigma_e$  operator to the CI Hamiltonian.

<sup>f</sup>CI+MBPT method, self-energy and screening correlations are included by  $\Sigma$  operators while valence-valence correlations are included by configuration interaction.

<sup>g</sup> $\Sigma_e$  in different waves are taken with factors to fit energies of a neutral atom.

<sup>h</sup>References [22,23].

TABLE II. Electron affinities of Ag and Au (eV). Comparison with other calculations and experiment.

Ag	Au	Ref.	Method
Theory			
1.008	1.103	[24]	Non-relativistic quadratic configuration interaction method
1.199	2.073	[24]	Relativistic quadratic configuration interaction method
1.254	2.229	[25]	Relativistic coupled cluster method
1.022		[4]	Non-relativistic stochastic variational method
	2.28	[26]	Fock-space relativistic coupled-cluster method
	2.26	[27]	Fock-space coupled-cluster method with Douglas-Kroll transformation (relativistic)
1.327	2.307		Present work
Experiment			
1.303	2.309	[28]	

TABLE III. Convergence of the calculation of the energies of  $e^+\text{Ag}$  and  $e^+\text{Au}$  with respect to the number of included partial waves (a.u.)

	$L_{\text{max}}$	CI <sup>a</sup>	CI + $\Sigma^b$	CI + $f\Sigma^c$
$e^+\text{Ag}$	0	-0.2232729	-0.2800223	-0.2729038
	1	-0.2271709	-0.2838360	-0.2749591
	2	-0.2309207	-0.2868375	-0.2765124
	3	-0.2350823	-0.2895691	-0.2780571
	4	-0.2388315	-0.2916800	-0.2793784
	5	-0.2419251	-0.2932381	-0.2804487
	6	-0.2443218	-0.2943470	-0.2812678
	7	-0.2460745	-0.2951085	-0.2818603
	8	-0.2472812	-0.2956100	-0.2822647
	9	-0.2480477	-0.2959189	-0.2825199
	10	-0.2484749	-0.2960829	-0.2826596
	11	-0.2486698	-0.2961444	-0.2827143
	12	-0.2487554	-0.2961682	-0.2827367
	13	-0.2487928	-0.2961778	-0.2827459
	14	-0.2488090	-0.2961817	-0.2827498
$e^+\text{Au}$	0	-0.2684049	-0.3500447	-0.3330163
	1	-0.2706582	-0.3526602	-0.3339500
	2	-0.2719813	-0.3539745	-0.3344564
	3	-0.2732705	-0.3550481	-0.3348765
	4	-0.2743905	-0.3558030	-0.3351787
	5	-0.2753222	-0.3563289	-0.3353973
	6	-0.2760539	-0.3566883	-0.3355525
	7	-0.2765943	-0.3569283	-0.3356590
	8	-0.2769686	-0.3570837	-0.3357294
	9	-0.2772074	-0.3571791	-0.3357333
	10	-0.2773390	-0.3572293	-0.3357972
	11	-0.2773925	-0.3572449	-0.3358049
	12	-0.2774146	-0.3572505	-0.3358078
	13	-0.2774239	-0.3572527	-0.3358091
	14	-0.2774278	-0.3572536	-0.3358095

<sup>a</sup>Standard CI method.

<sup>b</sup>CI+MBPT method, both core-valence and valence-valence correlations are included.

<sup>c</sup> $\Sigma$  is taken with fitting parameters as explained in the text.

TABLE IV. Positron binding by silver and gold calculated in different approximations (all energies are in a.u.)

	Neutral atom	Atom with $e^+$	$\Delta^a$
Silver			
CI	-0.22952	-0.24881	0.01929
CI + $\Sigma_e + \Sigma_p$	-0.28564	-0.29618	0.01054
CI + $\Sigma_e + \Sigma_p + \Sigma_{ep}$	-0.28564	-0.28843	0.00279
CI + $f\Sigma_e + f\Sigma_p + \Sigma_{ep}$	-0.27841	-0.28275	0.00434
Gold			
CI	-0.27461	-0.27743	0.00282
CI + $\Sigma_e + \Sigma_p$	-0.35536	-0.35725	0.00189
CI + $\Sigma_e + \Sigma_p + \Sigma_{ep}$	-0.35536	-0.35191	-0.00345
CI + $f\Sigma_e + f\Sigma_p + \Sigma_{ep}$	-0.33903	-0.33581	-0.00322

<sup>a</sup>Positron binding energy. Negative energy means no binding.

TABLE V. Energies (in a.u.) of Ag,  $Ag^-$ ,  $e^+Ag$ , Au,  $Au^-$  and  $e^+Au$  with respect to the energy of the core in relativistic and non-relativistic cases

	Neutral atom	Negative ion	Atom with a positron	Electron affinity	Positron binding energy <sup>a</sup>
Silver					
Non-relativistic	-0.2558	-0.2974	-0.2640	0.0416	0.0073
Relativistic	-0.2784	-0.3272	-0.2827	0.0488	0.0043
$\Delta$	0.0226	0.0298	0.0187	-0.0072	0.0030
Gold					
Non-relativistic	-0.2537	-0.3040	-0.2665	0.0503	0.0080
Relativistic	-0.3390	-0.4239	-0.3358	0.0849	-0.0032
$\Delta$	0.0853	0.1199	0.0693	-0.0346	0.0112

<sup>a</sup>Positive energy means bound state

TABLE VI. Comparison of the relativistic energy shift with other calculations (energies are in a.u.)

Atom/Ion	Present work	Schwerdtfeger and Bowmaker <sup>a</sup>
Ag	0.0226	0.0200
$Ag^-$	0.0072	0.0070
Au	0.0853	0.0714
$Au^-$	0.0346	0.0357

<sup>a</sup>Quadratic configuration interaction method, Ref. [24]

# FIGURES

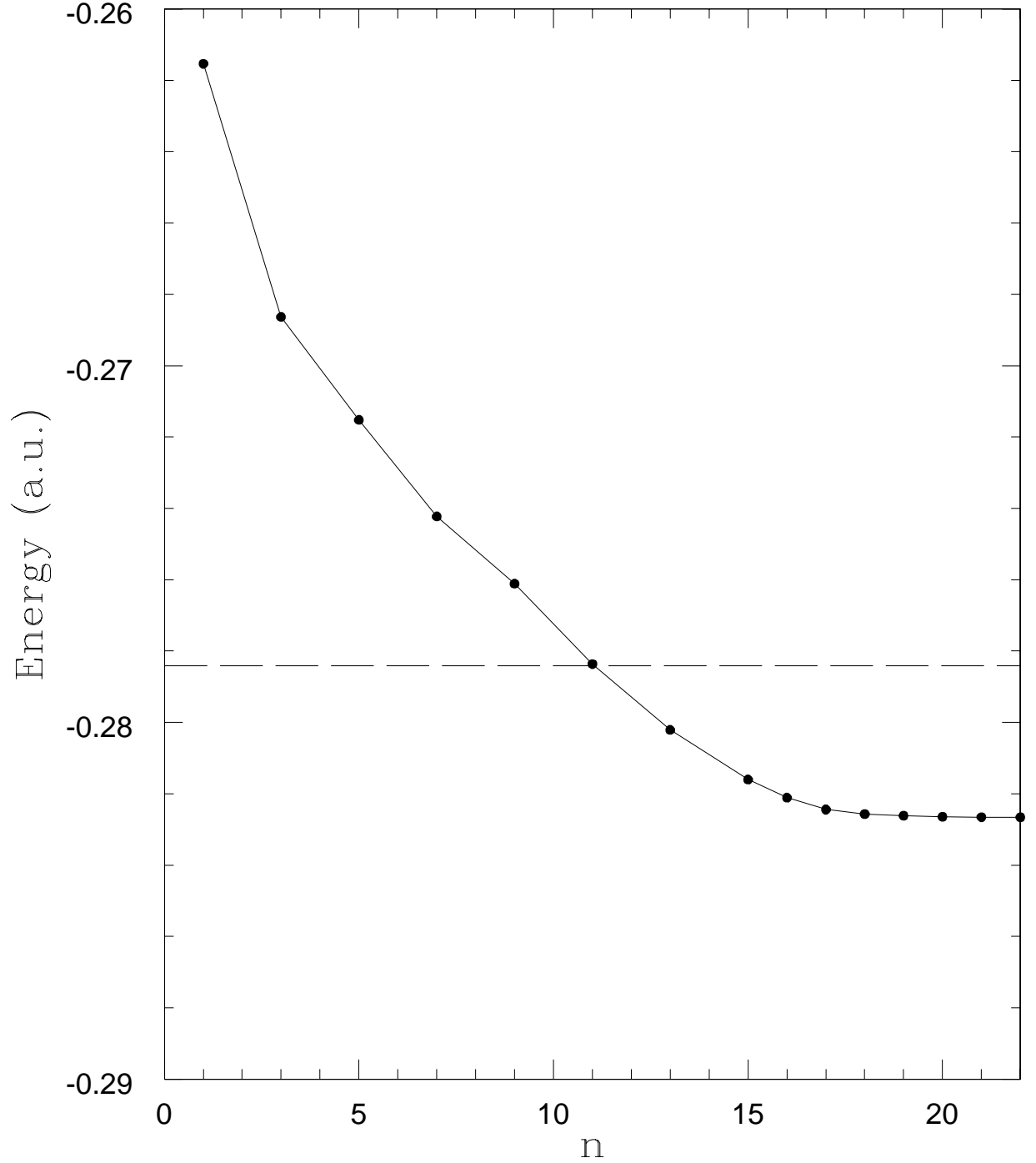


FIG. 1. Energy of  $e^+\text{Ag}$  as a function of the number of radial electron and positron basis functions in each partial wave ( $L_{\text{max}} = 10$ ) in the cavity with  $R = 30a_0$ . Dashed line represents the energy of neutral silver.

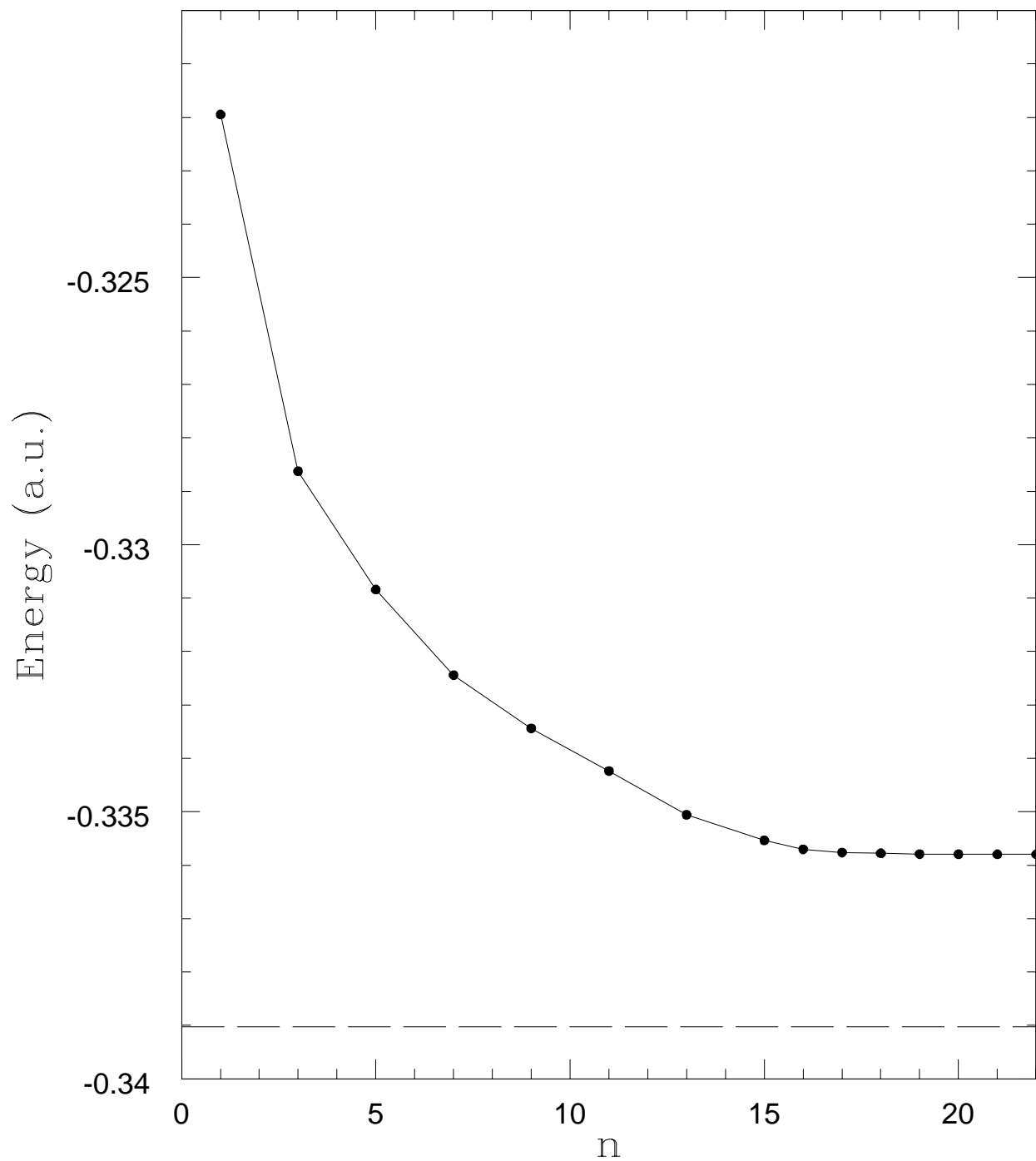


FIG. 2. Same as Fig. 1 but for  $e^+\text{Au}$ .